



Au NPs on anionic-exchange resin as catalyst for polyols oxidation in batch and fixed bed reactor

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ABSTRACT

Commercial weak basic anion resin (Dowex M-43) was used as support for gold nanoparticles (Au NPs). Au NPs stabilized by tetrakis(hydroxypropyl)phosphonium chloride (THPC) were immobilized on the support (Au_{THPC}/Dowex M-43). In alternative, Au NPs were generated by adsorbing NaAuCl₄ on the resin and then reduced by NaBH₄ (Au_{ads}/Dowex M-43). These catalysts were tested in the liquid phase oxidation of glycerol in a glass batch reactor: Au_{THPC}/Dowex M-43 showed better activity than Au_{ads}/Dowex M-43. The higher activity can be attributed to the smaller Au nanoparticles in Au_{THPC}/Dowex M-43 than Au_{ads}/Dowex M-43. Moreover Au_{THPC}/Dowex M-43 was tested in the glycerol oxidation in a fixed bed reactor showing good stability during the reaction time. All the catalysts have been characterised by TEM, FT-IR and XPS.

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1. Introduction

In the recent years, the conversion of renewable resources into high value chemical attracted a lot of attention [1–3]. As envisaged by the U.S. Department of Energy, there is the need to establish new starting materials which could clean out the dependency from fossil resources. Twelve molecules have been selected for finding new chemical platforms [4]. One of this is glycerol, obtainable in large quantities from biomass as a by-product of the transesterification of triglycerides. Glycerol is a highly functionalized molecule and a large number of useful compounds can be obtained through its oxidation, hydrogenolysis, dehydration, esterification, and/or polymerization [5–7]. As well as glycerol, carbohydrates such as glucose, sorbitol and fructose represent interesting starting materials. Glucose can be obtained in high amount from the decomposition of cellulose, primary product deriving from vegetable biomass [1,8]. Since Prati et al. reported that gold supported on activated carbon (AC) was catalytically active and selective for the oxidation of ethylene glycol to produce glycolate [9,10], gold as catalyst for such a type of liquid phase transformation has been subject of many studies [11,12]. In particular, it has been demonstrated that Au can be more active, selective and resistant to deactivation than Pd or Pt

for the selective liquid phase oxidation with O₂ as the oxidant of glucose to gluconic acid and of glycerol to glyceric acid [13–17]. The effect of the support on the catalytic activity has been extensively studied. Activated carbon is the most common and studied support for liquid phase reaction [16,18,19,9] but graphite [15,20] and metal oxides such as TiO₂ [21–24], CeO₂ [25–27], and Al₂O₃ [23,28], have been also largely used as support for gold nanoparticles. During the last few years, ionic-exchange resins [29–31] and polymer microgels [32,33] have been demonstrated to be an interesting class of supports for Au nanoparticles for liquid phase application. Biffis et al. reported that microgel stabilized gold nanoclusters show a higher activity than AC supported Au in the liquid phase oxidation of 1-phenylethanol, 1-octanol and 1-butanol, whereas Au nanoparticle prepared via metallic sol and supported on AC was more active for glucose oxidation [32]. Moreover Ishida et al. reported an interesting activity of different ion-exchange resins supported Au nanoparticles for glucose and 1-phenylethanol oxidation [29,31], showing that the catalytic activity is proportional to the basicity of the support used. In both cases the resin itself acted as stabilizer of the Au NPs. Thus, it is possible to tune size and morphology of the metal nanoparticles according to the structure of the support. In this work, we used Au nanoparticles supported on a weak anion-exchange resin (Dowex M-43) and applied these catalysts for the liquid phase oxidation of glycerol in a batch reactor. The catalysts have been prepared following two different procedures: the one immobilizing preformed metallic sol stabilized by tetrahydroxymethyl phosphonium chloride (THPC) [34], the second reducing with NaBH₄ the Au(III) salt adsorbed on the support.

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The two catalysts have been labeled respectively Au_{THPC}/Dowex M-43 and Au_{ads}/Dowex M-43. The catalytic test has been performed in a batch and in a fixed bed reactor as this latter configuration would help for industrial applications.

2. Experimental

2.1. Materials

NaAuCl₄·2H₂O (99.99% purity) and tetrakis(hydroxypropyl)phosphonium chloride (THPC) (98% solution) from Aldrich were used. NaBH₄ (purity >96%) and NaOH of the highest purity available were from Fluka. Gaseous oxygen from SIAD was 99.99% pure. Glycerol (88 wt% solution), glyceric acid and all the intermediates were obtained from Fluka. Anionic-exchanged resin Dowex M-43 was purchased from Dow Chemical and activated carbon X40S from Camel.

2.2. Catalyst preparation

2.2.1. Ionic exchange

An aqueous solution of HAuCl₄ (Au loading 1%) was added to the anion-exchange resin. The mixture was continuously stirred at room temperature for 2 h till the solution turned from pale yellowed to colourless. The resin was filtered and the solution was studied by inductive coupled plasma (ICP) in order to detect the total adsorption of Au on the support. The resin was redispersed in water and a solution of 0.1 M NaBH₄ (Au/NaBH₄ 1:4 mol/mol) was added to the solution under magnetic stirring. Finally, the resin was filtered and washed with water. The samples were dried at 80 °C for 2 h. The catalyst was labeled Au_{ads}/Dowex M-43.

2.2.2. THPC-protected gold sol

A freshly prepared solution 0.05 M of THPC was added (THPC/Au (w/w)=0.95) to a NaOH solution (10–3 M). After a few minutes NaAuCl₄ (10–3 M) was added dropwise, forming a brown metallic sol. An UV–vis spectrum of the gold sol was recorded, showing a complete reduction of Au(III) species. Within few minutes from their generation, the colloids (acidified at pH 2, by sulphuric acid) were immobilized by adding the support (Dowex M-43 and AC) under vigorous stirring. The amount of support was calculated in order to obtain a final metal loading of 1 wt% (on the basis of quantitative loading of the metal on the support). The catalysts were labeled Au_{THPC}/Dowex M-43 and Au_{THPC}/AC.

2.3. Catalytic test

2.3.1. Batch reactor

Reactions were carried out in a thermostated glass reactor (30 mL) provided with an electronically controlled magnetic stirrer connected to a large reservoir (5000 mL) containing oxygen at 3 atm. The oxygen uptake was followed by a mass flow controller connected to a PC through an A/D board, plotting a flow time diagram. 0.316 g of glycerol was dissolved in 4 mL of water, mixed with the desired amount of NaOH and the gold catalyst (0.3 M the final concentration of glycerol, glycerol/metal = 1000 mol/mol, NaOH/glycerol = 4 mol/mol). The reactor was pressurized at 3 atm of O₂ and thermostated at the appropriate temperature. Once the required temperature (50 °C) was reached, the gas supply was switched to oxygen and the monitoring of the reaction started. The reaction was initiated by stirring.

2.3.2. Fixed bed reactor

For the studies in a continuous fixed bed reactor a system similar to the reactor reported by Kimura [35] was used. A reactor made by Pyrex with an inner diameter of 10 mm and a height of 100 mm,

equipped with feed lines for aqueous solution of glycerol (5 wt%) (NaOH/glycerol = 1 mol/mol) and molecular oxygen, an output line and a water jacket for heating was used. Dioxygen flow was regulated by mass flow and set at 4 mL/min. The catalyst was packed in the reactor and glycerol solution and oxygen fed at a constant flow rate concurrently from the top of the reactor at a controlled temperature. The reactor was fixed vertically to avoid channeling.

Samples were removed periodically and analyzed by high-performance chromatography (HPLC) using a column (Alltech OA-10308, 300 mm × 7.8 mm) with UV and refractive index (RI) detection in order to analyze the mixture of the samples. H₃PO₄ 0.1 wt% solution was used as eluent. The identification of the possible products was done by comparison with the original samples.

2.4. Characterisation

2.4.1. Sol characterisation

UV–vis spectra of sols diluted in H₂O were recorded with HP8452 and HP8453 Hewlett-Packard spectrophotometers between 190 and 1200 nm, in a quartz cuvette.

2.4.2. Catalyst characterisation

- The metal content was checked by ICP analysis of the filtrate or alternatively directly on catalyst after burning off the carbon, on a Jobin Yvon JY24.
- Morphology and microstructures of the catalysts are characterised by TEM. The powder samples of the catalysts were ultrasonically dispersed in ethanol and mounted onto copper grids covered with holey carbon film. A Philips CM200 LaB₆ electron microscope, operating at 200 kV and equipped with a Gatan CCD camera, was used for TEM observation.
- Fourier transform-IR spectra were recorded with a Perkin Elmer 100 spectrometer using a mercury cadmium telluride (MCT) detector. Spectra with 4 cm⁻¹ resolution, 128 scans and a scan speed of 0.50 cm s⁻¹ were recorded at room temperature using CaF windows in the range 5500–450 cm⁻¹. The powders (KBr and sample) were pressed at 10 MPa for 10 min.
- X-ray photoelectron spectroscopy (XPS) measurements were performed using an M-Probe instrument (SSI) equipped with a monochromatic AlK_α source (1486.6 eV) with a spot size of 200 μm × 750 μm and a pass energy of 25 eV, providing a resolution of 0.74 eV.
- Nitrogen sorption measurements were performed using a Micromeritics ASAP 2010.
- Elemental analysis was performed using Perkin Elmer 2400.

3. Results and discussion

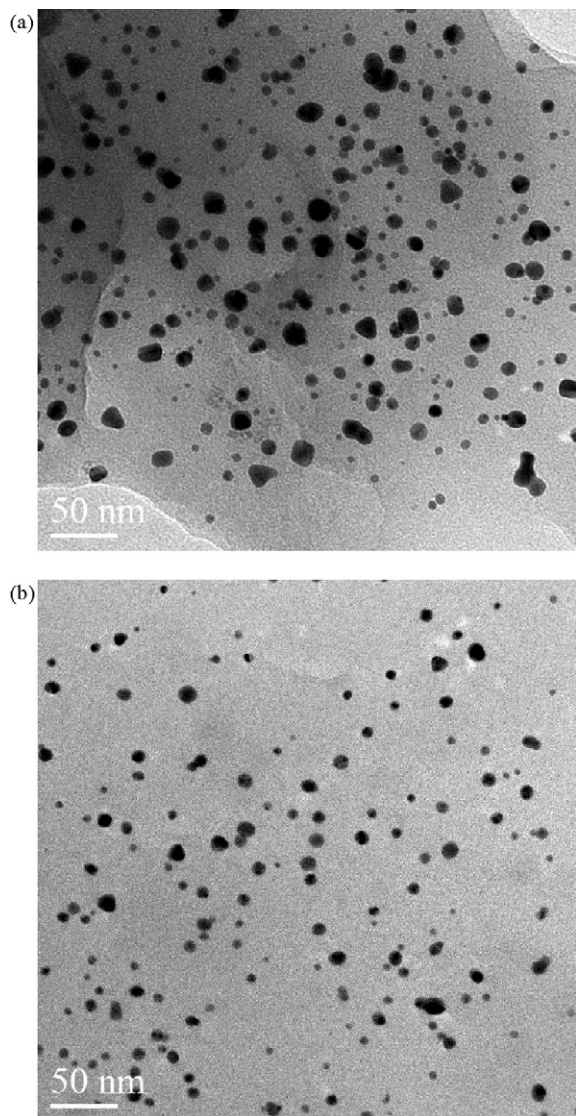
3.1. Catalyst preparation and characterisation

In this work, a weak base anion-exchange resin (Dowex M-43) was used as support for gold nanoparticles. Dowex M-43 (particle size distribution 300–1200 μm) is a commercial styrene-divinylbenzene macroporous resin with tertiary amino groups on the surface (Table 1). Two different synthetic routes were used to prepare the catalyst. In the first one, the AuCl₄⁻ ions were adsorbed on the resin by the interaction with the amino groups on the surface and then Au(0) NPs were formed by the reduction with NaBH₄. It has been reported that the amino groups can directly reduce Au(III) to Au(0) [29,36,37]. However this procedure leads to big Au nanoparticles especially in the case of macroporous resins, being the final size controlled by the morphology of the polymer [32]. Thus, in order to reduce the NPs dimension we speed up the Au reduction using a large excess of NaBH₄ (Au_{ads}/Dowex M-43). TEM analysis shows a good dispersion of Au nanoparticles on the support

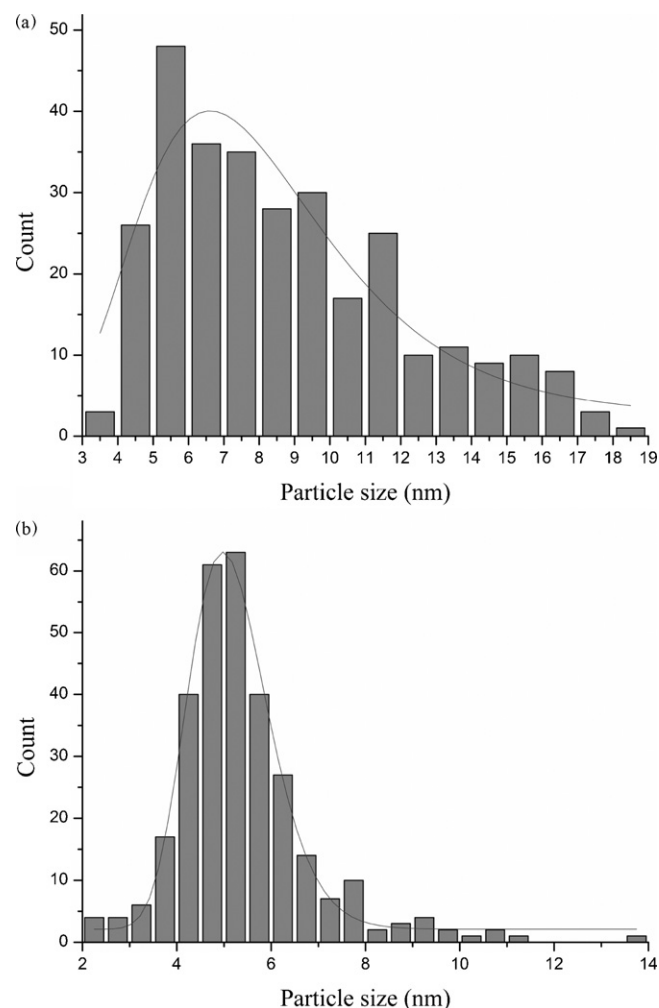
Table 1

Characterisation of the supports (AC and Dowex M-43) by nitrogen sorption measurements and combustion elemental analysis.

	Surface area (m ² g ⁻¹)	Average pore diameter (nm)	Elemental analysis (wt%)		
			C	N	H
AC	935	1.98	82	1	1
Dowex M-43	7	120	52	5	9

**Fig. 1.** TEM overview images of a) Au_{ads}/Dowex M-43 and b) Au_{THPC}/Dowex M-43.

(Fig. 1a). Au NPs have an average diameter of 8.78 nm. However, a wide diameter distribution was obtained (Table 2 and Fig. 2a). We can thus conclude that the amino groups on the surface of the Dowex M-43 are not effective in generating and stabilizing small gold nanoparticles even using NaBH₄ as reducing agent. Therefore

**Fig. 2.** Particle distribution of a) Au_{ads}/Dowex M-43 and b) Au_{THPC}/Dowex M-43.

a second catalyst Au_{THPC}/Dowex M-43 was prepared by immobilizing preformed Au NPs using THPC/NaOH as stabilizer and reducing agent. THPC is a good stabilizer for small nanoparticles, generating unsupported Au NPs around 2 nm [34,38]. The immobilization of Au_{THPC} NPs sol on Dowex M-43 generates a high metal dispersion even a growth of Au NPs size in comparison to the sol was observed (from 2 to 5.4 nm) as also previously observed with different sol [39]. A narrower particle size distribution was obtained (Table 2 and Fig. 2b) than in the case of Au_{ads}/Dowex M-43. For comparison,

Table 2

Statistical median and standard deviation of particle size analysis for Au catalysts.

Catalyst	TEM		XPS at.% Au(4f)/C(1s)
	Statistical media (nm)	Standard deviation σ	
1% Au _{ads} /Dowex M-43	8.78	3.39	1.6
0.96% Au _{THPC} /Dowex M-43	5.43	1.45	6.2
1% Au _{THPC} /AC	3.22	1.48	0.6
0.96% Au _{THPC} /Dowex M-43 after reaction	5.74	1.52	–

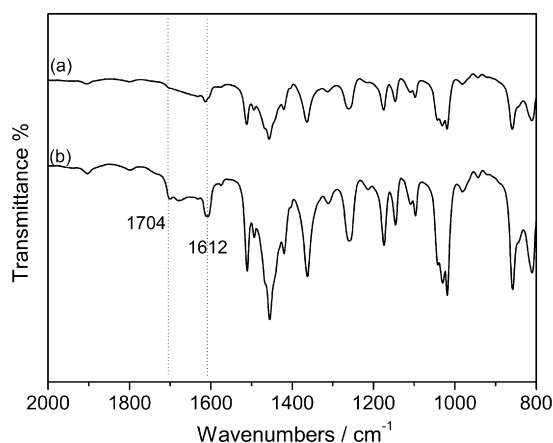


Fig. 3. FT-IR spectra of (a) Dowex/M-43 and (b) Au_{ads} /Dowex M-43.

Au_{THPC} NPS were also immobilized on AC, a classical support for liquid phase oxidation. When Au_{THPC} sol was immobilized on activated carbon X40S, smaller nanoparticles were observed (3.22 nm). Unfortunately this comparison could not be carried out for the Au_{ads} /Dowex M-43 catalyst as the adsorption of AuCl_4^- in the absence of a protective agent is reported to be not a good methodology for preparing Au/AC as very big particle sizes are obtained (<30 nm) [16].

XPS analysis was performed on Au_{THPC} /AC, Au_{ads} /Dowex M-43 and Au_{THPC} /Dowex M-43. As the C content of the supports differs greatly (by elemental analysis respectively 82% for AC and 56% for Dowex M-43 (Table 1)), to compare the at.% Au (%Au(4f)/C(1s)) revealed by XPS, normalized values have been used. The resulted values were 0.6, 1.6 and 6.2% respectively (Table 2). By considering the difference of particle diameters between Au_{THPC} /AC and Au_{THPC} /Dowex M-43 (3.20 and 5.43 nm respectively), we should expect an opposite trend: indeed it has been proved that bigger particles should show lower values of Au(4f)/C(1s) than bigger one [40]. We can then conclude that the result highlights a huge difference of the gold exposure on the surface (0.6 and 6.2 at.% Au(4f)/C(1s) respectively). The FT-IR spectrum of Au_{ads} /Dowex M-43 shows an absorption peak at 1612 cm^{-1} and a shoulder at 1704 cm^{-1} confirming the interaction between the nitrogen functionalities of the support and gold (Fig. 3). These bands were already observed after 2 h of adsorption of AuCl_4^- before the addition of NaBH_4 , confirming that Au^{3+} is partially reduced to Au^0 by the nitrogen functionalities present on the support according to Ishida et al. [29]. In fact they have reported the appearance of a new band at 1600 cm^{-1} and a shoulder at 1700 cm^{-1} when they used dimethylamino-functionalized resin as support and as reducing agent for Au NPs. The intensity of the absorption peak at 1630 cm^{-1} is also stronger than the one at 1710 cm^{-1} . We could then assign the band at 1630 cm^{-1} to N–H stretching band of a benzylamine and the peak at 1710 cm^{-1} to C=O of benzaldehyde. In fact, during the reduction of anionic Au(III) complex ion, together with the formation of $\text{Au}(0)$, iminium salt was formed. The decomposition

of the latter leads to the formation of the primary amine ($-\text{NH}_2$) of the benzylamine. The formation of an imine during the reduction of Au(III) followed by the decomposition of the iminium salt in water could also explain the benzaldehyde formation. This pathway of reduction could lead to the conclusion that the Au NPs interact initially with the amino groups of the resin. The subsequent addition of NaBH_4 accelerates the reduction of the anionic gold complex ion. This finding could support the hypothesis that Au NPs on Dowex are preferentially located near the N-containing groups.

3.2. Glycerol oxidation in batch reactor

Liquid phase oxidation of glycerol was performed in a pressurized glass reaction. Glycerol oxidation was performed at 50°C under basic conditions. Table 3 shows that, in terms of catalytic activity, Au_{THPC} /Dowex M-43 is more active than Au_{ads} /Dowex M-43 (TOF of 2098 and 763 h^{-1} respectively). Au_{ads} /Dowex M-43 showed a better selectivity to glyceric acid, the target product in comparison to Au_{THPC} /Dowex M-43 (64 and 60% respectively). This behavior is in agreement with previous findings: larger particle size resulted being more selective but less active than smaller one. Indeed, Au particle size is a crucial parameter to determine the activity and the selectivity in glycerol oxidation. It has been shown that small particles (3–5 nm) are more active than larger ones (8–30 nm) although larger particles give higher selectivity to glyceric acid [15,16,18,19,41]. Accordingly Au_{THPC} /AC (3.22 nm) appeared more active than Au_{ads} /Dowex M-43 (8.78 nm) [Table 3]. On the same basis, we expected a strong difference in terms of activity also between Au_{THPC} /AC (3.22 nm) and Au_{THPC} /Dowex M-43 (5.43 nm). Surprisingly, Au_{THPC} /Dowex M-43 showed almost the same activity as Au_{THPC} /AC (TOF of 2098 and 2164 h^{-1} respectively). Also the selectivity appeared similar, contrarily to what can be expected from the trend of particles size, apart from a slight preference for Au_{THPC} /AC for the consecutive oxidation of glyceric to tartronic acid (Scheme 1). A possible explanation could imply the different exposure of Au NPs. In fact, as highlighted before, the normalized at.% Au/C ratio revealed by XPS showed that Au_{THPC} NPs are located more on the surface in the case of Dowex M-43 than in AC. Thus, the shielding operated by the AC on Au NPs limits their activity. This shielding is not operating in the case of Dowex M-43, leading to a higher activity of Au NPs despite their larger dimension. Moreover the macroporous nature of the resin with respect to the microporous one of AC could facilitate the desorption of intermediates, thus decreasing the overoxidation of glyceric to tartronic acid (Scheme 1).

3.3. Glycerol oxidation in fixed bed reactor

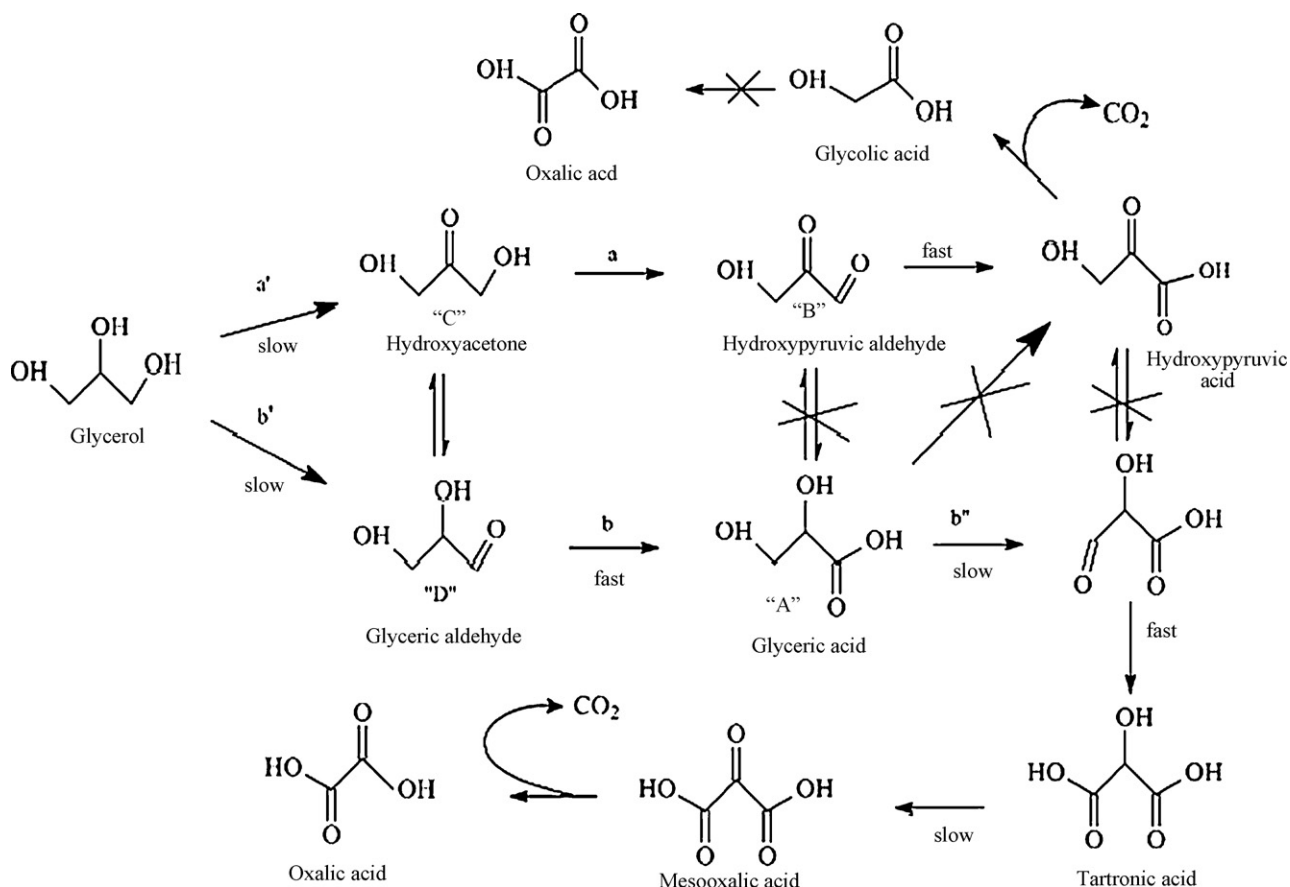
As Au_{THPC} /Dowex seems to be a promising catalyst for the liquid phase oxidation of polyols in batch reactor, we tested this catalyst also in a fixed bed reactor, a more convenient methodology from an industrial point of view. Kimura's group was the first in 1993 to report the use of a fixed bed reactor for the liquid phase oxidation of glycerol, using Pt–Bi supported on granular charcoal catalyst with dihydroxyacetone as main product [35]. More

Table 3
Catalytic performance of Au based catalysts in batch reactor.

Substrate	Catalyst	Selectivity					TOF (h^{-1}) ^b
		Glyceric acid	Glycolic acid	Oxalic acid	Tartronic acid	Hydroxypyruvic acid	
Glycerol ^a	Au_{ads} /Dowex M-43	64	28	2	6	–	763
	Au_{THPC} /Dowex M-43	60	30	2	8	–	2098
	Au_{THPC} /AC	50	30	3	16	1	2134

^a Reaction conditions: glycerol 0.3 M, 4 eq. NaOH, 3 atm O_2 , 50°C , metal/substrate 1/1000 (mol/mol). Selectivity calculated at 90% of conversion.

^b Calculation of TOF based on total metal.



Scheme 1.

recently, Hutchings' group reported glycerol oxidation in multi-phase structured reactors with Au on activated carbon as catalyst [36]. Davis' group studied the influence of the reactor configuration (batch and fixed bed reactor) for the glycerol oxidation using Au/TiO₂ catalyst, and focusing on the effect of reaction conditions without any study on the stability of the catalyst [42]. In this work, we tested Au_{THPC}/Dowex M-43 in the liquid phase oxidation of glycerol in a continuous system with the aim to study the stability of the catalyst for possible industrial applications. The reaction was carried out at 50 °C with Liquid Hourly Space Velocity (LHSV) of 0.092 h⁻¹, using 10 g of catalyst. After 2 h, the system reached the steady conditions and no obvious deactivation was observed in the following 20 h (Fig. 4). ICP analysis showed that no leaching of Au during the reaction occurred. Furthermore, TEM showed that the morphology of the catalyst did not change and only a slight growth of Au NPs was observed from 5.43 nm for the fresh catalyst to 5.74 nm after reaction (22 h), probably due to some agglomeration (Fig. 5). In terms of selectivity we observed a selectivity of 40% to glyceric acid and 25% to tartronic acid at 22% of conversion, remaining constant during the 22 h of reaction, confirming that the catalyst

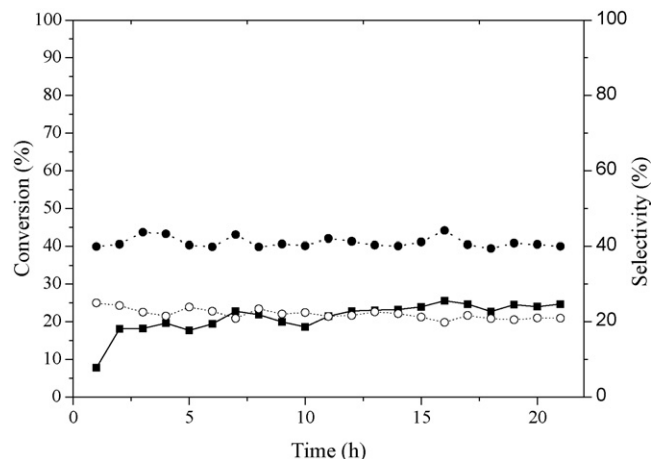


Fig. 4. Catalytic performance of Au_{THPC}/Dowex M-43 in fixed bed reactor. Reaction conditions: glycerol 5 wt%, glycerol/NaOH 1:1 (mol/mol), O₂ flow 4 mL/min, LHSV 0.092 h⁻¹. Glycerol conversion (■), glyceric acid selectivity (●), and tartronic acid selectivity (○).

Table 4

Effect of NaOH amount on catalytic performance of Au_{THPC}/M-43 in batch reactor.

NaOH/glycerol ratio	Selectivity ^a						TOF (h ⁻¹) ^b
	Σ Glyceric + tartronic acid	Glyceric acid	Tartronic acid	Oxalic acid	Glycolic acid	Hydroxypyruvic acid	
1	65	49	16	13	20	2	415
4	68	60	8	2	30	–	1768
1 (fixed bed)	65	43	22	12	18	6	–

Reaction conditions: 0.3 M alcohol, 3 atm O₂, 50 °C, metal/substrate 1/1000 (mol/mol).

^a Selectivity calculated at 90% of conversion.

^b Calculation of TOF based on total metal.

Table 5

Effect of glycerol flow on the activity and selectivity of Au_{THPC}/M-43 during continuous glycerol oxidation.

LHSV (h ⁻¹)	Conversion	Selectivity					
		Σ Glyceric + tartronic acid	Glyceric acid	Glycolic acid	Oxalic acid	Tartronic acid	Hydroxypyruvic acid
0.023	40	57	31	22	18	26	3
0.046	31	60	37	20	15	23	5
0.092	22	64	42	18	12	22	6
0.183	12	61	44	19	12	17	8
0.368	8	63	50	19	11	13	7

Reaction conditions: glycerol 5 wt%, glycerol/NaOH 1:1 (mol/mol), O₂ flow 4 mL/min.

did not change obviously its morphology. Comparing the results of batch and fixed bed reactors, we noted that the overall selectivity to glyceric and tartronic acid two consecutive products (Scheme 1) almost remains constant (68% vs 65%). The only difference lies on the different glyceric acid/tartronic acid ratios: in batch reactor we observed a main contribution of glyceric acid. Thus, we ascribed this difference to the different NaOH/glycerol ratios. To confirm

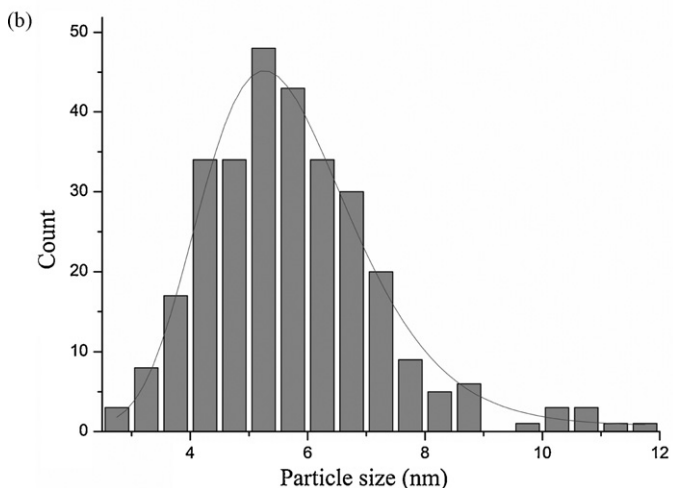
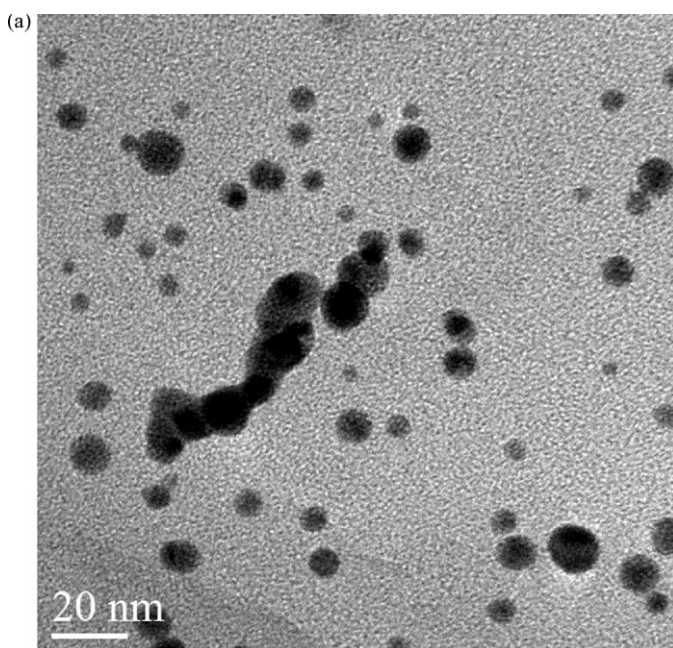


Fig. 5. a) TEM overview and b) particle distribution of Au_{THPC}/Dowex M-43 after reaction in fixed bed reactor.

this point, we performed a batch test using only 1 eq. of NaOH; and we obtained the same selectivity as in the fixed bed reactor (Table 4). Conversely, we also varied the LHSV (Table 5) by changing the glycerol solution flow, using the same catalyst. Each LHSV test was maintained for 22 h. As reported in Table 5 reducing the contact time reactant/catalyst, i.e. increasing the LHSV, the selectivity to glyceric acid increases. However, the overall selectivity to glyceric acid plus tartronic acid remained constant.

Summing up the results from batch and flow reactor, we concluded that the selectivity of the reaction using the same catalyst can be tuned by varying the reaction conditions (contact time and amount of base): the increasing of the contact time reactant/catalyst promotes consecutive reactions as well as the decreasing of base amount. Therefore an increasing of base amount (NaOH) apparently facilitates the desorption of glycerate, thus reducing its consecutive oxidation.

4. Conclusion

Two different catalysts were prepared by direct deposition of Au NPs and the immobilization of Au THPC protected NPS onto the commercial weak base resin Dowex M-43. TEM results showed that using THPC sol immobilization, it is possible to obtain Au NPs around 5 nm whereas with adsorption larger particles have been obtained. When tested in the liquid phase glycerol oxidation in batch reactor, Au_{ads}/Dowex M-43 showed low activity probably due to the large particles size (~9 nm), whereas Au_{THPC}/Dowex M-43 was as active as Au_{THPC}/AC in spite of the larger particles size (5.40 nm) than on AC (3.22 nm). This behavior can be addressed to the higher at.% of Au on the surface of Dowex M-43 (XPS) with respect to that measured on AC. Moreover the macroporous nature of Dowex M-43 could favour the desorption of products, thus decreasing consecutive reactions. The comparison between batch and continuous (fixed bed) reactions on Au_{THPC}/Dowex M-43 also revealed that the enhanced selectivity to primary oxidized product can be obtained both by decreasing the contact time and by increasing the base amount.

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